Effect of carbon on the microstructure and sliding wear performance of CoCrMo matrix composites from room temperature to 1000 °C

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\textbf{Abstract}
This work aimed to fabricate the CoCrMo matrix composites with different carbon contents, and the carbon content was optimized to achieve the good mechanical and tribological properties from room temperature to 1000 °C. Four composites containing different carbon content (0, 0.3 wt.%, 0.6 wt.% and 1 wt.%) were fabricated by powder metallurgy technology. Microstructure and tribological properties were studied. Friction behaviors were conducted on a disc-on-ball tribotester rubbing against Si$_3$N$_4$ ball. The carbon greatly improved the wear resistance of CoCrMo matrix composites due to the strengthening effect of carbides (Cr$_3$C$_2$ and Mo$_2$Co$_5$C) and the dense oxides film. However, the friction coefficient slightly increased. There was a critical value of carbon content for hardness and high-temperature friction and wear behaviors. The composite with 0.6 wt.% carbon had the most favorable tribological behaviors from RT to 1000 °C. Four composites showed different friction mechanisms.

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\section{Introduction}

Cobalt matrix materials are important superalloys, which are widely used for high-temperature wear service as some key parts [1–4]. Stellite alloys are an essential part of cobalt alloys. Many researchers used different elements to reinforce the mechanical properties, corrosion resistance and microstructure of cobalt alloys such as boron, tungsten and molybdenum [5–7]. Especially, the carbon is considered the first strengthening phase for the alloys [8,9]. Normally, the content of carbon in matrix is about 0.1–3 wt.%. The carbon element can form different types of carbides in matrix due to carbon content, metal element and fabricated method, including M$_2$C$_3$, M$_2$C, M$_6$C, etc. (M is the metal element) [10]. According to the carbon content, the cobalt alloys are divided into different commercial grades. The size, phase and content of carbides obviously influence the microstructure and mechanical properties of cobalt alloys [3,10]. Sometimes, the brittle carbides can reduce the mechanical properties of alloys [11]. The variation of mechanical properties can greatly influence the wear resistance of cobalt alloys. And therefore, the optimization of carbon content in cobalt alloys is inevitable in order to balance...
the wear resistance and mechanical properties of cobalt alloys at different conditions.

Cobalt alloys have outstanding antioxidation, high temperature mechanical properties and wear resistance in comparison with nickel matrix superalloys. In view of this, the wear behaviors of cobalt matrix alloys were widely investigated in order to provide the reference [6,12,13]. The tribological properties of Stellite alloys were reported when the testing temperature is below 600 °C, for example, Stellite 6, 12 and 21 [13–15]. The investigation found that the wear resistance of alloys derived from the high hardness at low temperature. At high temperature, the metal elements were oxidized. These oxides formed oxides film on the contact surfaces. Herein, the wear resistance of cobalt alloys was dependent on the high temperature oxidation of different elements [16,17]. And therefore, the alloy showed poor tribological properties at low temperature. In other words, the tribological properties of cobalt matrix alloys focused on the wear rules. In order to reinforce the tribological properties of cobalt alloys from low temperature to high temperature, some positive measures had been taken. Radu and Li et al. [18,19] added yttrium element into the Stellite alloys. The research results indicated that the yttrium could strengthen the hardness of alloys because of the formation of compound containing yttrium element. At high temperature, the Y2O3 increased the compactness of oxide film on the contact surfaces. And therefore, the wear resistance of modified Stellite alloys had obviously improvement. Zhen [20] fabricated Stellite 6 coating with NbC and h-BN and investigated the tribological properties at room temperature. High hardness and lubricating effect of h-BN improved the friction and wear of Stellite 6 coating on steel. Carbon fiber was also used to increase the wear resistance of Stellite 21 alloys at room temperature [11]. The fine fiber particles could form graphite film on the contact surfaces. However, carbon fiber maybe react with metal elements and lose the advantage of carbon fiber. Although ceramic particle and metal oxides were reported as strengthening phase in the cobalt alloys [21,22], the hard ceramic particle had a negative effect on the friction coefficients of materials. According to the previous reports, the influence of carbon on the wear and friction behaviors of cobalt alloys is rarely done at high temperature (1000 °C).

In this study, Co-Cr-Mo was used as matrix of composites. Different contents of carbon were added into the matrix, and the composites were fabricated by powder metallurgy technology in a furnace. The carbon content in matrix was optimized. The relationship of content, microstructure and tribological properties was investigated. The wear behaviors were conducted by a disc on ball tribotester from RT (24 °C) to 1000 °C. Moreover, tribological mechanisms of composites were discussed.

2. Experimental procedure

2.1. Preparation of composites

The sizes of cobalt, chromium, molybdenum and carbon were about 60 μm, 50 μm, 70 μm and 35 μm, respectively. The powders were the commercial grade, and the purity belonged to analytical pure. The composition of composites was listed in Table 1. CMC0, CMC1, CMC2 and CMC3 represented the four composites. Four composites were sintered by P/M in a vacuum sintering furnace. The corresponding powders were well mixed by using a high energy ball mill machine for 8 h at a speed of 250 rpm according to the formula of table. The obtained uniform powders were put into a graphite model. When the temperature of furnace rose to 1200 °C at a rate of 15 °C per minute, the mixed powders were sintered at a pressure of 35 MPa for 50 min in the vacuum atmosphere (10⁻² Pa). The composites were naturally cooled to RT when the sintered process was finished, and then the specimens were machined into the proper size.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC0</td>
<td>74.0</td>
<td>16</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>CMC1</td>
<td>73.7</td>
<td>16</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>CMC2</td>
<td>73.4</td>
<td>16</td>
<td>10</td>
<td>0.6</td>
</tr>
<tr>
<td>CMC3</td>
<td>73.0</td>
<td>16</td>
<td>10</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Fig. 1 – Set-up of high-temperature tribotester.

2.2. Evaluation of tribological tests

The high temperature friction and wear behaviors of four composites were performed on a HT-1000 tribotester with a configuration of ball to disc in air (see Fig. 1). The operation mode of tribotester is rotation. Si3N4 ceramic ball was chosen as the tribocouple (Hv: 15 GPa, diameter: 6 mm) which was fixed during the friction process, and the discs was made of composites with a dimension of φ 26 mm × 4 mm. Before tests, the testing surfaces of composites were polished to 0.35 μm by a grinding machine and cleaned by acetone. The rotational speed was 0.20 m/s, and the testing load was 10 N; the rotational radius was 5 mm. The testing temperature points were 24 °C (room temperature)-1000 °C, the internal of temperature was 200 °C. The duration of each test was 20 min. The computer software recorded the real-time friction coefficient of four composites. Each testing points were done four times to ensure the accuracy of experimental data.

The microhardness of four composites were determined by using a MH-5 hardness instrument with a load of 300 g...
and a dwell time of 10 s. The Archimedes drainage principle was used to test the actual density of obtained composites. Three measurements were repeated for each parameter. Microstructure morphologies and surfaces of wear tracks were analyzed by scanning electron microscope (JEOL, IT-300) and EDS (X-MAX-50). The cross section profiles of wear tracks for obtained composites were tested by using a surface profiler. The phases of all composites were investigated by XRD (DIFFRACTOMETER-6000). The wear rates of obtained composites equaled the total wear volume (mm³) divide by the normal load (N) and sliding distances (m), and the unit was mm³/N.m. The formula was:

\[
w = \frac{V}{F \cdot S}
\]

(1)

Each experimental point was tested three times and reported the average value.

3. Results and discussion

3.1. Microstructure, phase and physical properties of materials

Fig. 2 gives the XRD patterns of obtained composites. During the high temperature sintering process, Cr and Mo atoms go into the crystal Co lattice because of solid state reaction. Co, Cr and Mo elements form the γ phase of face centered cubic. When the sintering temperature decreases, part of γ (FCC) phase transfers into the low temperature stable ε phase of close-packed hexagonal [5,23]. And therefore, the main phases of obtained composites are two allotropes: γ (FCC) and ε (HCP). With the addition of carbon, the diffraction peaks of composites are gradually changed. The XRD patterns of CMC1, CMC2 and CMC3 are different from that of CMC0. Carbon element fully reacts with other metal elements and forms two types of carbides: Cr₇C₃ and intermediate compound of Mo₂Co₃C. The diffraction intensity increases when the carbon content increases. It means that the amount of Cr₇C₃ and Mo₂Co₃C increases. According to the XRD patterns of composites, the phases of CMC1, CMC2 and CMC3 are composed of γ (FCC), ε (HCP), Cr₇C₃ and Mo₂Co₃C. The possible reactions are follows:

\[
7\text{Cr} + 3\text{C} \rightarrow \text{Cr}_7\text{C}_3
\]

(2)

\[
3\text{Mo}+3\text{Co} + \text{C} \rightarrow \text{Mo}_2\text{Co}_3\text{C}
\]

(3)

The backscatter electron image of typical microstructure and EDS element distribution maps of specimens CMC0 and CMC2 are given in Fig. 3. Composition of CMC1, CMC2 and CMC3 is similar, so the microstructure of CMC2 is only given. CMC0 and CMC2 show the similar microstructure (see Fig. 3a and b). There is no crack and hole on the surfaces. It means that the structure of obtained composites is compact. All elements of composites uniformly distribute in the matrix. The light grey area is the Mo-rich phase. The carbon simple substance is not found through the matrix, suggesting the carbon forms compounds with other elements at high temperature. The result corresponds to the XRD pattern (see Fig. 2).

Table 2 lists the density, hardness and porosity of four composites. It can noted that the carbon content influences the micro-hardness of specimens. The formation of carbides reinforce the hardness of specimens as strengthening phase in matrix during the solidification [9,11]. The carbides can hinder the movement of dislocation. So the hardness of specimens increase. The amount of carbides is dependent on the carbon content. When the amount of carbides is low, the carbides can enter into the metal particles, which plays an important role in improving microhardness of specimens. However, the amount of carbides increases in order that carbides
aggregate the interface of metal particles [10,24]. The continuity of matrix is destroyed. Additionally, the carbides has the brittle mature. Consequently, CMC3 shows the lower hardness than those of other specimens. Low density of carbon results in the decrease of sintered density of composites. Four composites keep the low porosity, suggesting the high compactness of specimens.

3.2. Wear and friction behaviors

The friction coefficients of obtained composites with testing temperature rubbing against Si$_3$N$_4$ ball are illustrated in Fig. 4. It is notable that the friction coefficients of four composites decrease when the testing temperature rises from 24 °C–1000 °C. The temperature has an obvious effect on the
Table 2 – Micro-hardness, density and porosity of obtained composites.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Hardness</th>
<th>Density (g/mm²)</th>
<th>Porosity</th>
</tr>
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<tbody>
<tr>
<td>CMC0</td>
<td>485</td>
<td>8.59</td>
<td>1.02%</td>
</tr>
<tr>
<td>CMC1</td>
<td>512</td>
<td>8.50</td>
<td>0.93%</td>
</tr>
<tr>
<td>CMC2</td>
<td>523</td>
<td>8.42</td>
<td>0.94%</td>
</tr>
<tr>
<td>CMC3</td>
<td>468</td>
<td>8.30</td>
<td>0.96%</td>
</tr>
</tbody>
</table>

Fig. 4 – Vibration of friction coefficients of obtained composites with temperature at 10 N and 0.20 m/s.

friction coefficients of composites [16,17]. The friction coefficients of CMC1, CMC2 and CMC3 increase when the carbon content increases in the matrix. CMC3 shows the highest friction coefficient at all testing temperatures. However, CMC0 keeps the lowest friction coefficient. The corresponding friction mechanism will be discussed below.

Fig. 5 gives the wear rates of four composites rubbing against Si₃N₄ ball at 0.20 m/s and 10 N at different testing temperatures. The wear rates of four composites have the similar trend, which increase with the increase of temperature, and then decrease. Their only difference is the temperature point of peak value for wear rate. The peak value of CMC0 and CMC1 is at 600 °C. However, the wear rates of CMC2 and CMC3 reach up to the maximum values at 400 °C. CMC1, CMC2 and CMC3 have the lower wear rates than CMC0. It suggests that the carbon effectively improves the wear resistance from 24 °C to 1000 °C, especially, at elevated temperature. Meanwhile, the wear resistance of composites containing carbon is generally strengthened with increasing carbon content. When the carbon content is 1 wt%, the wear rate of CMC3 increases. From 24 °C to 1000 °C, the CMC2 shows the lowest wear rate. The wear rates of specimen without carbon are 1-6 times higher than those of CMC2. At 24 °C, 800 °C

Fig. 6 – XRD patterns of worn surfaces of CMC2 at 600 °C and 1000 °C.
and 1000 °C, the wear rate of CMC2 is 3.3–5.6 × 10⁻⁶ mm³/N.m, the specimen shows excellent wear resistance.

From 24 °C to 1000 °C, testing temperature and carbon content influence the wear and friction behaviors of four composites. Metal elements could be oxidized and generated complicated compounds [17,19,23]. At low temperature, the amount of oxides is low (see Fig. 6), plus the tribocouple scrape the wear track. Oxides film does not form on the surfaces. At elevated temperature, the amount of oxides increases (see Fig. 6), which form dense oxides film on the surfaces (see Fig. 7) [19,25,26]. These oxides film can separate tribocouples during the testing process. Furthermore, the in situ generated molybdates (CrMoO₃ and CoMoO₄) are also high-temperature solid lubricants which can provide lubricating effect to the specimens [25,27]. Therefore, the friction coefficients and wear rates is low at elevated temperature. Above 400 °C, ε (HCP) transfers into the γ (FCC), which results in a decrease in the hardness of materials [10]. At the same time, the wear track does not covered by the complete oxides film. Based on these reasons, the wear rate increase. The hard carbides phase, MoO₃ and Cr₂O₃ scrambles the contact surfaces of tribocouple, resulting in the increase in the friction coefficient of composites [27]. This trend becomes more and more obvious with the increase of carbon content. On the other hand, the carbides phase in matrix can support the external load and improve the hardness. Thus, the wear resistance of composites is enhanced. For the reason that the wear rates of CMC3 with 1.0 wt.% increases. There are two reasons: first, carbide phase Cr₇C₃ is easily oxidized when it suffers from cyclic stress of high temperature [11,24]. The crack generates at the places of carbide in matrix; Second, The specimen CMC3 has a low hardness. And therefore, the wear rate of CMC3 increases at testing temperature. Generally speaking, the composite with 0.60 wt.% carbon has

![Fig. 7 – SEM imagine of oxides film on the wear track.](image)

![Fig. 8 – SEM morphologies of wear tracks of four composites at room temperature: (a) CMC0, (b) CMC1, (c) CMC2 and (d) CMC3.](image)
the most reasonable friction coefficients and wear rates than other composites from room temperature (24 °C) to 1000 °C.

3.3. Analysis of wear tracks

Fig. 8 illustrates the worn morphologies of different composites at room temperature rubbing against ceramic ball. It can be seen that the morphologies of four composites are similar. Ploughing, wear debris and plastic deformation are found on the contact surfaces. Additionally, the amount of wear debris increase with the increase in carbon content. Wear debris containing hard particles cuts the contact surfaces as third-body and causes the ploughing on the surfaces as well as the increase of friction coefficients at 24 °C. It suggests that the abrasive wear is the wear mechanism of four composites. Fig. 9 gives the worn morphologies of four composites at 600 °C. The wear tracks of specimens CMC2 and CMC3 are smooth as compared to those of specimens CMC0 and CMC1 at the same conditions. The surfaces of CMC0 and CMC1 are characterized by ploughing, plastic deformation and oxidation (see Fig. 9a and b). The result manifests that the specimens suffer from serious wear at 600 °C, which agree with the wear rates of composites. Meanwhile, the oxides film does not fully cover the wear tracks. CMC0 and CMC1 show the mixed patterns of abrasive wear, plastic deformation and slight oxide wear. The CMC2 and CMC3 have the high hardness or carbides content in order that the specimens have high plastic deformation resistance, and can support the oxides film on the surface. The percentage of oxides film is more than those of CMC0 and CMC1 (see Fig. 9c and d). It is concluded that the wear mechanism of CMC2 and CMC3 is slight abrasive wear and oxidation wear.

Fig. 10 shows the worn surfaces of four composites at 1000 °C sliding against ceramic ball. At high temperature, the wear debris and materials are oxidized (see Fig. 11) and the oxidation rate speeds up. These oxides form dense oxides film on the worn surfaces, and the oxides film fully covers the worn surfaces of four composites at 1000 °C [19,25], which is proofed in Fig. 7. Not only does this oxides film reduce the wear rates and friction coefficients of composites at elevated temperature [16,27], but it can also prevent materials further oxidation. The ploughing is noted on the wear tracks of four composites. It means that he dominant of wear mechanisms is oxidation wear and slight abrasive wear.

![Fig. 9 - SEM morphologies of wear tracks of four composites at 600 °C: (a) CMC0, (b) CMC1, (c) CMC2 and (d) CMC3.](image-url)
Fig. 10 – SEM morphologies of worn surfaces of four composites at 1000 °C: (a) CMC0, (b) CMC1, (c) CMC2 and (d) CMC3.

Fig. 11 – EDS analysis of the oxides film on the surface of CMC3 in Fig. 10c.

Fig. 12 gives the SEM morphologies of countersurfaces of CMC2 at different temperatures. The wear debris is transferred to the surfaces of Si₃N₄ and forms transferred layer. When the testing temperature increases, the transferred layer becomes more and more continuity and compactness. The composition of transferred layer is similar with that of oxides film on the worn surfaces of CMC2 according to EDS analysis of the transferred layer (see Figs. 11 and 13). Because of the existence of this transferred layer, the wear of specimen to ball changes into the wear of oxides film to transferred layer. Specimens and counterpart avoid the wear from room temperature to 1000 °C during sliding.
4. Conclusions

1) The carbon reacted with other elements and formed Cr$_7$C$_3$ and Mo$_3$Co$_3$C in the matrix. Phases of composites are composed of $\gamma$(FCC), $\kappa$(HCP), Cr$_7$C$_3$ and Mo$_3$Co$_3$C. The hardness increases due to the strengthening effect of carbides. However, excess carbides aggregated at the interface of metal particles, which decreased the hardness.

2) Carbon content and temperature greatly influenced friction coefficients and wear rates of four composites. Carbides increased the wear resistance and friction coefficient of composites. The carbide Cr$_7$C$_3$ was easily oxidized at elevated temperature, and crack generated. The wear resistance of composites reduced as carbon content rose. The dense oxides film was formed on the wear tracks.

3) The CMC2 containing 0.60 wt.% carbon had the most favorable tribological behaviors from room temperature to
1000 °C. It ascribed to the oxides film containing in situ generated solid lubricants of CrMoO₃ and CoMoO₄ and high hardness.

4) At low temperature, four composites were characterized by abrasive wear along with slight oxidation wear. The oxidation wear and slight abrasive wear were the wear mechanisms of four composites at elevated temperature.

**Conflicts of interest**

The authors declare no conflicts of interest.

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